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Design, Efficiency and Materials for Carbon/Air Fuel Cells

Direct Carbon Fuel Cell Workshop

NETL, Pittsburgh PA

by

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Topics

- Efficiency:
  - Coulombic and electrochemical
- Design considerations
  - Specific challenges
  - Advantages relative to MCFC
- An angled cell for particulate fuel
- A rigid block fuel cell for distributed power
- Considerations of efficiency of fuel production
- Considerations of cost
- Research and development emphasis

Brief Summary of Electrons/Mole of Graphitic Carbon Anodes

Conditions	Method used	Results	Reference
T = 700 C, graphite, carbonate	ΔW, $dV/dt \sim I/nF$	n = 4	Tamaru & Kamada [1935]
T = 400-900 C, graphite, CO_3^{2-}	dV/dT, CO/CO_2	n = 4	Hauser [1964]
T = 700-800 C, turbostratic,coke	dV/dt, some ΔW	n = 4	Weaver [1977-9]
T = 700 C, CO_3^{2-} various carbons	$d[CO_2]/dt = I/nF$	n = 4	Vutetakis [1984]
T = 900-1100 C, $NaAlF_4 + Al_2O_3$, turbo & graphite	$d[CO_2]/dt = I/nF$	n = 4	Haupin; [1981]

The defining reaction is $C + O_2 = CO_2$

High Efficiency Derives from a Favorable Cell Thermodynamics

Fuel	Theoretical limit = $\Delta G^o(T)/\Delta H^o_{std}$	Utilization efficiency, μ	V(i)/V(i=0) = ε_v	Actual efficiency = $(\Delta G/\Delta H^o_{std})(\mu)(\varepsilon_v)$
C	**1.003**	**1.0**	**0.80**	**0.80**
CH_4 [a]	0.895	0.80	0.80	0.57
H_2	0.70	0.80	0.80	0.45

Efficiency of a fuel cell or battery is defined:

≡ (electrical energy out) / (Heat of combustion (HHV) of fuels input)

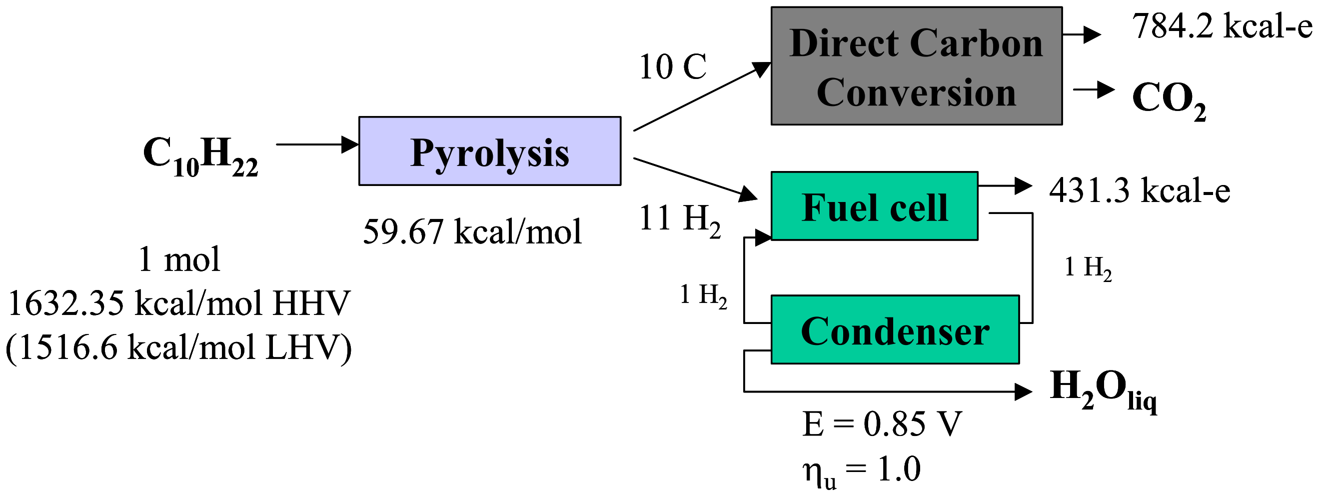
= [theoretical efficiency G/H][utilization fraction μ][voltage efficiency ε_v]

$= [\Delta G(T)/\Delta H^o][\mu][V/V^o] = [\mu][nFV]/\Delta H^o$

--where $\Delta G(T) \equiv -nFV^o \equiv \Delta H - T\Delta S$

Typical C/air efficiency is 80%
Degraded by energy cost of fuels production

The pyrolysis of fuel oil followed by fuel cell conversion yields highest potential efficiency



- Without waste heat recovery: ε = 72% ΔH_{std} = 77% LHV (modeled as decane)
- System is <u>mechanically simple</u> without reforming or heat engines
- Pyrolysis consumes 3.6% of the HHV of fuel oil
- Efficiency increased to >80% LHV by recycling waste heat to pyrolyze fuel oil

This approach uses H_2/SOFC in simplest, most robust form
Avoids the entropy increases associated with gasification
Mechanically simple

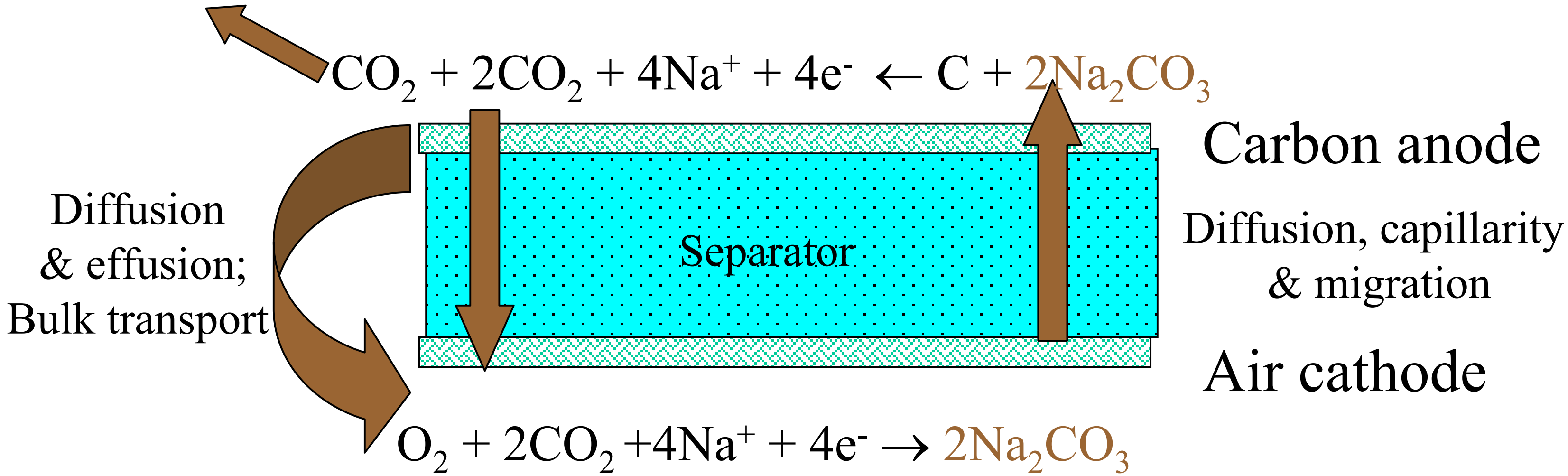
DCFC: Unique Set of Difficult Challenges

- Transport of carbon solids into cells
  - Pneumatic or salt pumping for large systems
  - Low rate of anode fuel volume transfer: 1:4000 ~ solid:H_2
- All fuel in operating cell must be subject to continuous polarization of ~ 20 mV to avoid Boudouard reaction
  - But no losses on standby
  - Requires electrodrodes to be thin pastes or shielded blocks
- Sulfur emerges as toxic COS or COS_2
- Spalling corrosion limits metals for construction or current collection
  - Graphitize cells and anode current collectors
- Trade: higher cost ash-free carbons for cleaned coal
  - Engineering of salt recovery

DCFC: Some Simplifying Aspects, Too

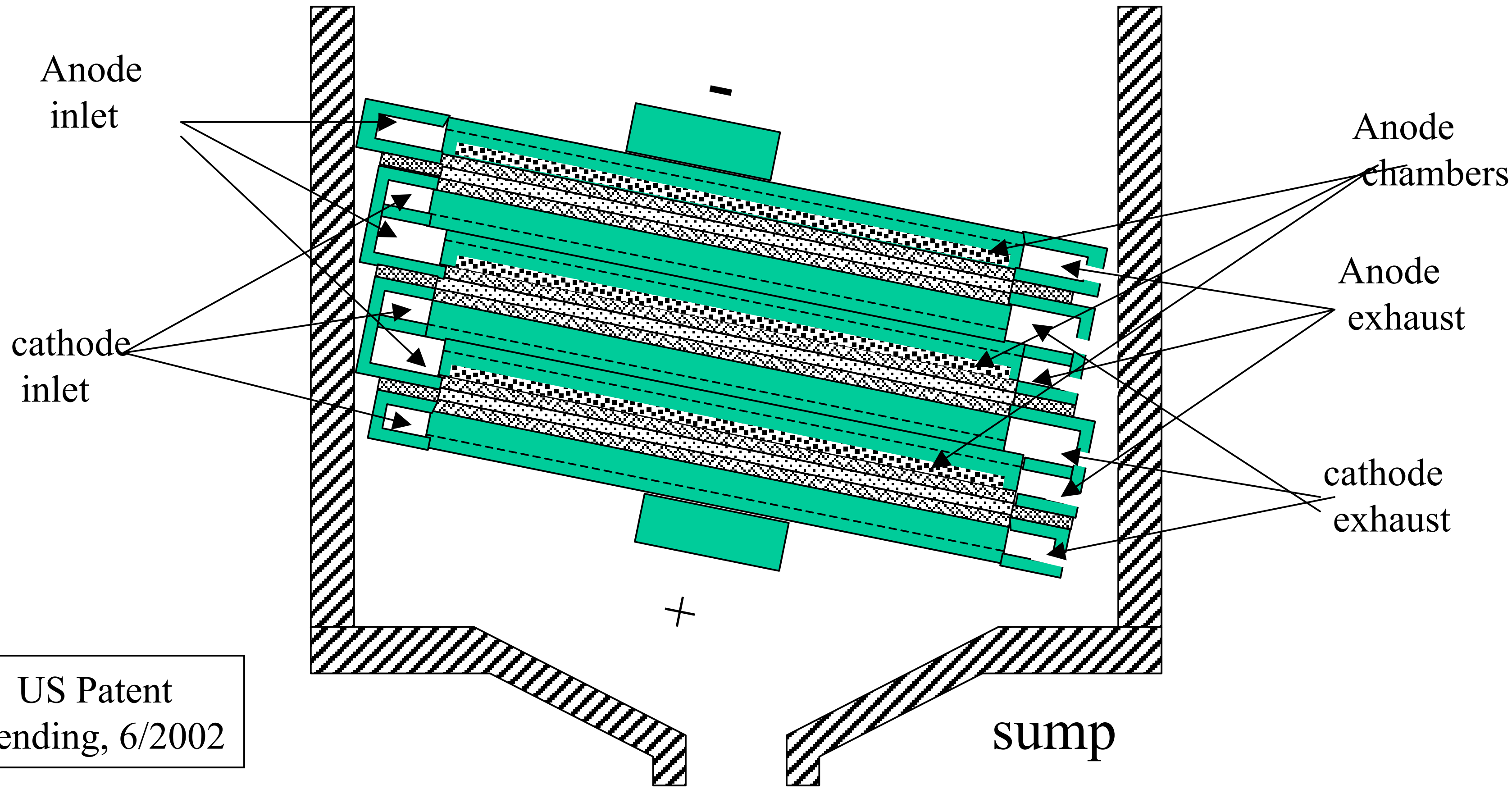
- Fixed C, CO_2 activities:
  - very large anodes, fixed potential, full utilization in single pass
- C/melt slurry or paste is not-explosive in air
  - Relaxes demands on cell and separator for isolation of fuel and air
- Anhydrous fuels: no steam corrosion, embrittlement
- Higher T: non-Li salts, hydraulic salt recovery
- Carbonate flux: protects separator, collector
- Solvent extracted carbons: salt lasts life of cell
  - cleaned coal ~ month
- Mechanical simplicity: low S swing, no need for bottoming cycles
- As truck fuel: no fuel storage problem

Protection of Separator by Salt Flux



- Molten salt continuously generated at cathode
  - Separator protected by flux $= 2(i/4F)$
- Should offset degradation of separator by coal-entrained solids

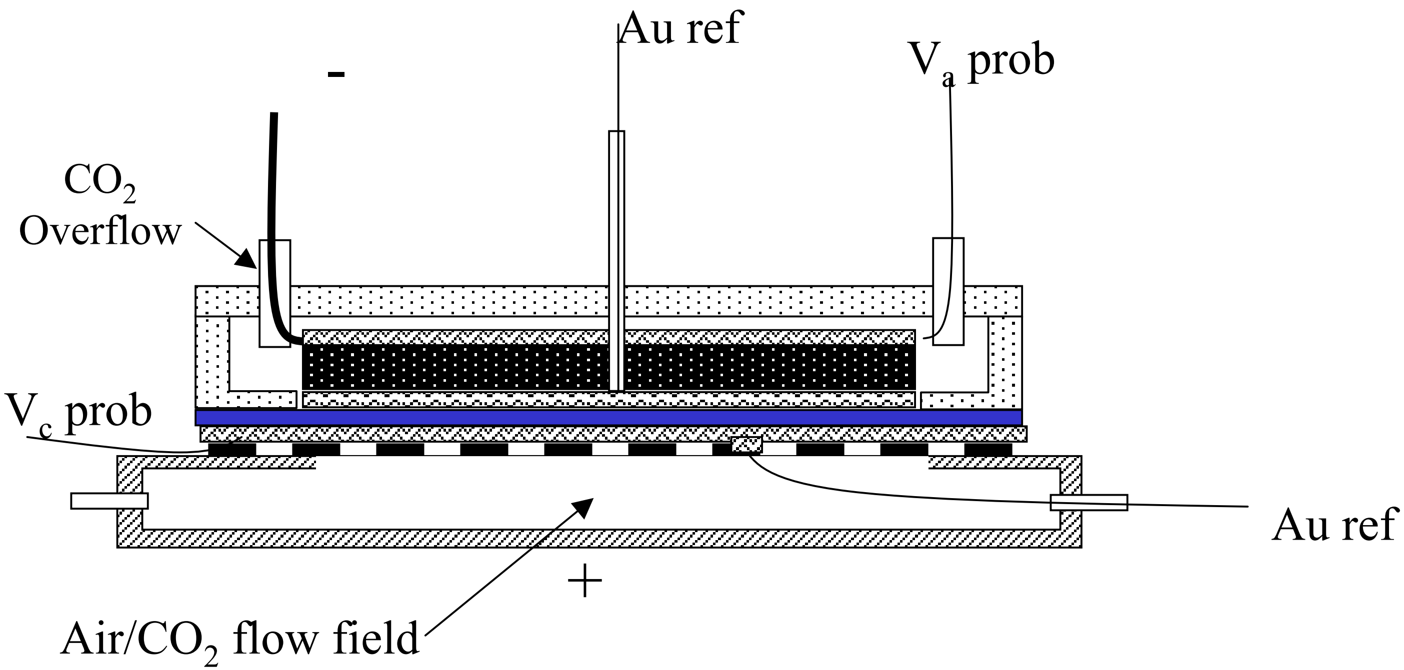
Tilted Configuration Controls Electrolyte Wetting and Flooding



US Patent Pending, 6/2002

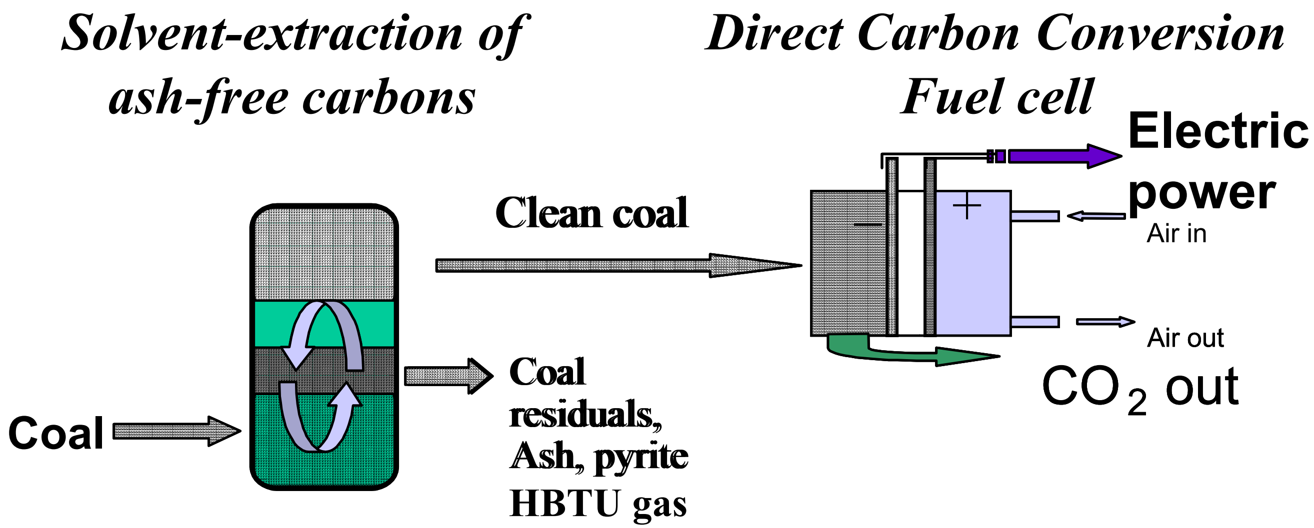
- Allows periodic replacement of electrolyte
- Maintains constant anode wetting as fuel is converted

Experimental Approach: Idealized Fuel Cell Geometry, Full Diagnostics for Rigid Plate Anodes

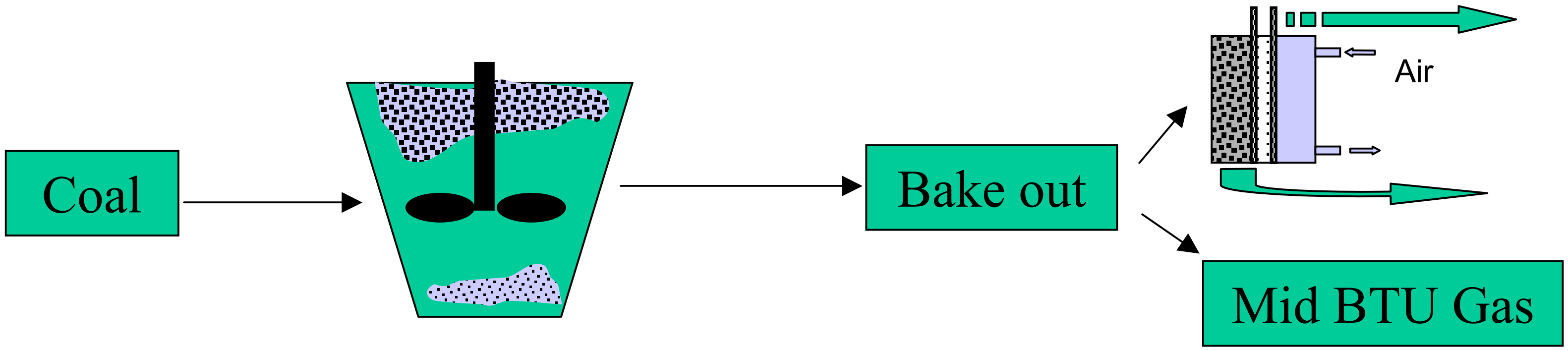


- **Independent reference electrodes and voltage probes**
- **Determine anode off-gas composition as function of current, temp**
- **Isolation of reaction zone in rigid carbon block**

Extraction and Use of Carbon from Coal



Hydraulic Cleaning of Coal



Pulverization and
Hydraulic Separation
from Ash & Pyrite

- Hydraulic separation of C (<1 % S, ash) from pyrite, ash
  - 65 kWh/ton (98 % retention of heating value)
  - Net coal-to-electricity efficiency 78 %
- Total cost \$60/ton => 0.8 ¢/kWh
- But: high ash requires further cleaning or periodic electrolyte exchange

Ref.: B. K. Parekh, U. Kentucky

How Often Must Electrolyte Be Replaced?

- Assume electrolyte equal mass to carbon fuel
- Assume electrolyte can tolerate 0.25 g-ash/cm^2
- Rate of carbon fuel additions: 1 kA/m^2 ~ 0.25 g/cm^2-day
- Interval between electrolyte replacement/recycle
  - *0.5% ash— hydraulic cleaned coal* *200 days (twice yearly)*
  - *0.05% ash—solvent extracted coal* *5.5 years (life of cell)*
  - *0.01% ash—pyrolyzed oil* *N/A*

• For common fuels under consideration, cost of electrolyte exchange is insignificant
• Lowest recycle cost if Na/K eutectic is used

Summary: Efficient Processes for Cleaning Coal

- UK: hydraulic separation
  - grind to 30 µm; baking to remove mid-BTU gas; low-ash product
- UK-process: extraction of pitch with anthracene oil
  - 425 ºC, 200 atm; no hydrogenation; 40-70% yield; 0.05-0.1 % ash
- WVU-process: extraction of pitch with n-methyl pyrrolidone
  - Ambient pressure, 200 ºC; 40-50% yield; 0.05-0.1 % ash

Process	***Efficiency***	***Yield***	***%Ash***	***%S***	***Cost***
UK-hydro	98%?	100%	0.5-1	1-2	\$60/ton, \$3/GJ 0.8 ¢-fuel/kWh
UK-solvent	?	40-70%	0.05	0.5	\$200/ton, 2.4 ¢-fuel/kWh
WVU-solvent	?	40-50%	0.05	0.5-1	\$78-140/ton, 1-2 ¢-fuel/kWh

Recommended R&D

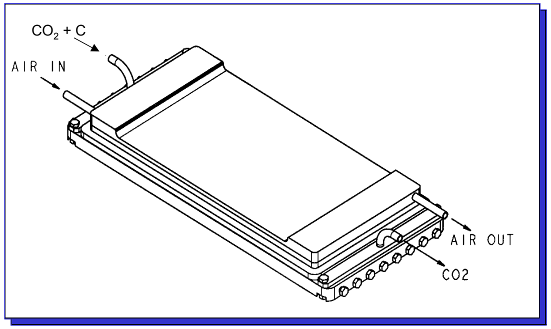
- Engineering of refueled system on ~ 1 kW scale for generic C
- Develop cell materials (e.g., highly graphitic carbon) that resist sulfur corrosion at 650-750 °C
- Management of ash and melt recovery
  - Systems level
  - CO_2 feed to air stream? May not be required
- Re-examination of solvent extraction for fuels production
  - Radically different constraints from advanced materials production
- Adaptation of MCFC cathodes and catalysts for DCFC.

Priority R&D Emphasis:
Move rapidly to 1 kW demonstrations using multiple technologies

Initial Hardware Cost Estimates

Stack cost ~\$250/KW at 2 kW/m^2

Component or factor	Basis	Cost \$/kW
Zirconia fabric	Zircar, Inc. retail price \$200/m^2	100
Nickel felt	Eltech, Inc. \$20/m^2 retail price	10
Stainless steel lid	Ni plated SS frame, \$5/lb	38
Graphite base, collector	\$1.00/lb design	10
Assembly	20% parts	32
G&A, profit	20% parts and labor	48
Total		\$237



Sources of power	Capacity in kilowatts	Cost to build/kW
Coal-fired plant	300,000-400,000	\$900-1,300
Advanced gas turbine	400,000-1,000,000	\$650-900
Internal combustion generator	500-5,000	\$400-625
Microturbine	25-300	\$450*-750
Fuel cell	2-3,000	\$500*-3,000
Wind power	700-5,000	\$1,000-1,500
Solar panels	1-500	\$1,500*-6,500

*Target cost, if production cost declines as projected

Source: Electric Power Research Institute